IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Takaaki MAEKAWA et al.	:	Docket No. 2001-1159A
Serial No. 09/913,736	:	Group Art Unit 1724
Filed October 31, 2001	:	Examiner Peter A. Hruskoci
METHOD OF REMOVING PHOSPHORIC ACID CONTAINING WASTEWATER	:	

VERIFICATION OF TRANSLATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, the undersigned, hereby declare as follows:

1. I am familiar with the Japanese and English languages, and am capable of translating faithfully from Japanese to English.

2. The attached translation is faithful English translation of Japanese Application No. 1999-041970 filed February 19, 1999.

3. I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

August 21,2003
(Date)

Toshio Nishizawa
(Signature of translator)
Toshio NISHIZAWA

JP-A-2000-237763

[Title of the Invention]
Method of removing phosphoric acid contained in wastewater

[Abstract]
[Problem] Addition of calcium is made easy to remove phosphoric acid in wastewater.
[Solving Means] Calcium or calcium and magnetite are inclusively fixed on a polymer solid and brought in contact with wastewater, and calcium apatite is prepared by reaction with the phosphoric acid in the wastewater to remove phosphoric acid.

[Claims]
[Claim 1]
A method of removing phosphoric acid contained in wastewater, wherein calcium is inclusively fixed on a polymer solid and brought in contact with wastewater, and calcium apatite is prepared by reaction with the phosphoric acid in the wastewater.
[Claim 2]
A method of removing phosphoric acid contained in wastewater, wherein calcium and magnetite are inclusively fixed on a polymer solid and brought in contact with wastewater, and calcium apatite is prepared by reaction with the phosphoric acid in the wastewater.
[Claim 3]
The method according to claim 1, comprising mechanically shaking

the polymer solid containing calcium to control the surface adhesion and diffusion of calcium.

[Claim 4]

The method according to claim 2, comprising mechanically or electromagnetically shaking the polymer solid containing calcium and magnetite to control the surface adhesion and diffusion of calcium.

[Claim 5]

The method according to claim 1 or 2, comprising recovering calcium apatite prepared in running water.

[Claim 6]

The method according to claim 3 or 4, comprising recovering calcium apatite prepared.

[Claim 7]

An inclusively fixed carrier for removing phosphoric acid in wastewater, wherein calcium is supported on a polymer solid.

[Claim 8]

The carrier according to claim 5, wherein magnetite is contained in the polymer solid.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The invention of the present application relates to a method of removing phosphoric acid in general domestic wastewater, industrial wastewater and the like. More specifically, the invention of the present application relates to removal of phosphoric acid from various wastewaters such as domestic wastewater, which are discharged from food

industries, production fields in agriculture and the like.

[0002]

[Prior Art and Problems thereof]

The concentration of phosphoric acid in domestic wastewater is about 2 to 3 mg/L, but the removal of phosphoric acid in domestic wastewater is an important object for preventing eutrophication of rivers, lakes and marshes together with the necessity for removing phosphoric acid from the wastewaters of food industries, production fields in agriculture and the like.

[0003]

Studies for removing phosphoric acid have been promoted hitherto for the object. There is proposed a method for reacting phosphoric acid in a solution, which contains calcium excessively, to remove phosphoric acid. However, since the conventional method is a method of adding a calcium solution by a pump or the like to wastewater containing phosphoric acid, there has been a problem that calcium cannot be easily added in domestic drainage canals.

[0004]

[Means for Solving the Problems]

The inventor of the present application has originated a method of gradually diffusing calcium by a carrier including calcium and adding it to wastewater in a drainage canal, in order to solve the problems of a prior art as describe above and to make it easy to add calcium in wastewater. Namely, the present invention provides first a method of removing phosphoric acid contained in wastewater, wherein calcium is inclusively fixed on a polymer solid and brought in contact with

wastewater, and calcium apatite is prepared by reaction with phosphoric acid in wastewater.

[0005]

Further, the present invention provides second a method of removing phosphoric acid contained in wastewater, wherein calcium and magnetite are inclusively fixed on a polymer solid and brought in contact with wastewater, and calcium apatite is prepared by reaction with phosphoric acid in wastewater. Then, the present invention provides third the first method comprising mechanically shaking the polymer solid containing calcium to control the surface adhesion and diffusion of calcium, provides fourth the second method comprising mechanically or electromagnetically shaking the polymer solid containing calcium and magnetite to control the surface adhesion and diffusion of calcium, provides fifth the first or second method comprising recovering calcium apatite prepared in running water, and provides sixth the third or fourth method comprising recovering the prepared calcium apatite.

[0006]

Furthermore, the invention of the present application provides seventh an inclusively fixed carrier for removing phosphoric acid in wastewater, wherein calcium is supported on a polymer solid, and provides eighth an inclusively fixed carrier, wherein magnetite is contained in the polymer solid.

[0007]

[Mode for Carrying Out the Invention]

The present invention has characteristics as described above,

and embodiments of the invention will be described below. The invention employs an inclusively fixed carrier in which calcium is supported on a polymer solid, in order to remove phosphoric acid in wastewater. The polymer solid in this case can more preferably contain magnetite, and may be various solids so far as they are superior in the supportability of calcium. For example, there are used a polymer having anionic groups such as a hydroxyl group and a carboxyl group, and various other polymers. Suitable examples of the polymer solid include polyvinyl alcohol (PVA), a partially esterified polymer thereof, poly(acrylic acid), a partially esterified polymer thereof, starch powder, a partially acetylated body thereof, and other polysaccharides.

[0008]

It is not always necessary that magnetite provides magnetism to the polymer, and magnetite is contained in the polymer so that the carrier can be moved or shaken by the magnetic field generated by magnetic field generating means (for example, an electro-magnet or permanent magnet) arranged at the outside of a wastewater treatment vessel or a wastewater treatment region. These magnetites may be powder of ultra paramagnets and the like which are not mutually adhered when the magnetic field does not exist. For example, they are powder of metal oxides of iron and the like.

[0009]

With respect to the method of the present invention and the fixed carrier therefor, it is indicated as one aspect that supported calcium is reacted with phosphoric acid in waste waster on the surface of the fixed carrier or in a state in which it is dispersed in a liquid to

prepare calcium phosphate, namely calcium apatite, which is separated and recovered as crystals. Since there is a possibility that the diffusion of calcium is inhibited in a state in which calcium phosphate crystals are adhered on the surface of the carrier, the adhesion of the crystals on the surface of the carrier can be prevented, for example, by covering the fixed carrier (1) with a net (2) having a large hole diameter as shown in FIG. 1 and mechanically shaking it in a treatment vessel (3). Further, the adhesion of the crystals on the surface of the carrier can be similarly prevented in such a manner that magnetite is contained in the carrier of the polymer solid and the magnetic field is varied by the surrounding electro-magnets (4) to be shaken as shown in FIG. 2.

[0010]

From the viewpoint of controlling the diffusion speed of calcium, the diffusion speed can be also controlled by shaking the carrier by these methods. The calcium apatite crystals obtained can be utilized as a fertilizer and the like, and therefore it is desirable to recover them by a simpler method so as not to discharge them from a drainage canal. Various procedures are considered for the means. For example, as shown in FIG. 3, the calcium apatite crystals (7) can be easily separated from wastewater to be recovered by providing a precipitation vessel (6) at the terminal end portion of the drainage canal (5) as FIG. 3 and periodically collecting them. The dispersion or diffusion of calcium from the fixed carrier can be controlled by the concentration of PVA as the polymer of the fixed carrier and the like, the concentration of calcium, the thickness of the fixed carrier, the

shaking speed of the fixed carrier, etc. It is indispensable to prevent inhibition to calcium diffusion in case where the reaction on the surface of the carrier occurs. The recycle of calcium phosphate as a fertilizer by a periodical recovery operation is possible by diffusing calcium in the carrier by a forced shaking, accumulating calcium apatite, which is a reaction product, in the precipitation vessel, and periodically collecting it. Hereat, the polymer carrier containing calcium shall be periodically exchanged.

[0011]

Further, in the example of FIG. 3, the calcium-containing polymer carrier (1) is charged in a cage (8) or the like which is easily shaken, and immersed in a place where the wastewater of the drainage canal (5) flows, the precipitation vessel is provided at its post-stage, and the cage (8) or the like is designed to be able to be mechanically or electrically shaken. However, the method is not limited to the example. The fixed carrier may be a fixed bed or a flowing bed together with the establishment of an appropriate processing condition.

[0012]

Then, examples are shown as follow to more specifically illustrate the present invention.

[0013]

[Examples]

(Example 1)

Method of preparing fixed carrier containing calcium

With respect to the carrier of calcium, one (weight ratio) of calcium hydroxide or caustic lime per one of acetylated starch is

kneaded, the mixture is extruded by a molding machine to be spheres or pellets having a size of 5 to 10 mm to be prepared, and this is dropped in a 10 to 15% PVA solution to be covered with a thin film.

[0014]

It is appropriate that the average molecular weight of PVA is about 2000 and the degree of saponification is 95% or more. A 10 to 15% by weight of PVA solution is prepared to be used. Since the PVA molecule in an aqueous solution has a nature of discharging water molecule from the polymer structure and enforcing the structure when freezing and thawing are repeated, the nature is utilized. Specifically, the PVA solution is frozen at a low temperature of about -20℃ for 24 to 48 hours, the polymerization of PVA is promoted by repeating this operation 2 to 3 times, and the physical strength is enhanced. The acetylation substitution degree of the acetylated starch and the size of porous gels of the PVA polymer which are obtained by the operation control the discharge speed of calcium ion.

[0015]

Further, since arginic acid ion has a nature of forming a polymer by being bonded with calcium ion to be made insoluble, the nature can be used for covering the surface of the polymer solid. Specifically, the above-mentioned polymer solid is dropped in a 0.5 to 5% by weight of arginic acid solution, or the 0.5 to 5% by weight of arginic acid solution is sprayed on the surface of the polymer solid and this is dropped in a saturated solution of calcium chloride. The calcium arginate thus prepared is insoluble in water, a coating film is prepared on the arginate by the 10 to 15% PVA solution, and freezing is repeated

2 to 3 times at a low temperature of about -20℃ to prepare the fixed carrier containing calcium.

[0016]

When magnetite is used, it is desirable that 1.5 to 3.0 g of magnetite is preliminarily mixed in 50 to 100 mL of the PVA solution before polymerization by freezing or the like and the mixture is used.

(Example 2)

An inclusive fixed carrier was prepared by supporting calcium as in Example 1. A solution having an initial concentration of phosphoric acid of 3 mg/L was treated using the carrier.

[0017]

FIG. 4 shows the relation between the treatment time and the variation of the concentration of phosphoric acid in case of not adding calcium chloride as seed crystals, and FIG. 5 shows that in case of adding seed crystals. As a result, it was confirmed that the concentration of phosphoric acid can be set to about 0.1 to 1 mg/L. Thus, a removal rate of about 80% to 90% can be expected because the concentration of phosphoric acid is usually about several mg/L in a domestic drainage canal. Even if the concentration of phosphoric acid is higher than several mg/L, it is considered that the final concentration is about 0.5 mg/L.

[0018]

[Effect of the Invention]

According to the present invention, there are obtained superior effects that (1) the addition of calcium can be easily carried out by inclusively fixing calcium on a polymer, (2) the surface adhesion and

diffusion of calcium can be controlled by electrically or mechanically shaking the polymer containing magnetite, and (3) the calcium apatite crystals can be separated and recovered from wastewater by periodically recovering them at a precipitation vessel provided at the terminal end portion of the drainage canal, and the reutilization of calcium phosphate as a fertilizer becomes easy, in the crystallization operation of selectively removing phosphoric acid in wastewater in the drainage canal.

[Brief Description of Drawing]

[FIG. 1]

FIG. 1 is a sectional view exemplifying a system of mechanical shaking.

[FIG. 2]

FIG. 2 is a sectional view exemplifying a shaking system using an electro-magnet.

[FIG. 3]

FIG. 3 is a schematic view of the construction exemplifying a treatment system in which a precipitation vessel is provided.

[FIG. 4]

FIG. 4 is a view showing an example of a treatment result in case where no seed crystal exists.

[FIG. 5]

FIG. 5 is a view showing an example of a treatment result in case where seed crystals exist.

[Description of Codes]

1 Fixed carrier

2 Net

3 Treatment vessel

4 Magnet

5 Drainage canal

6 Precipitation vessel

7 Calcium apatite crystals

8 Cage

FIG. 3

Calcium-containing polymer

[Amendment for procedure]

[Filing Date] December 20, 1999

[Amendment 1]

[Name of Document Subjective for Amendment] Specification

[Name of Items Subjective for Amendment] Whole statement

[Method for Amendment] Change

[Content of Amendment]

[Name of Document] Specification

[Title of the Invention]

Method of removing phosphoric acid contained in wastewater

[Scope of Claims for Patent]

[Claim 1]

A method of removing phosphoric acid contained in wastewater, wherein an inclusively fixed carrier in which calcium is inclusively fixed on a polymer solid having an anionic group is brought in contact with wastewater, and calcium is diffused from the inclusively fixed carrier to prepare calcium apatite by reaction with the phosphoric acid in the wastewater.

[Claim 2]

The method of removing phosphoric acid contained in wastewater according to claim 1, wherein calcium or calcium hydroxide is kneaded with acetylated starch to be molded, and then the inclusively fixed carrier in which calcium is inclusively fixed on a polymer solid by coating a polyvinyl alcohol film is brought in contact with the wastewater.

[Claim 3]

The method of removing phosphoric acid contained in wastewater according to claim 2, wherein the inclusively fixed carrier in which calcium is inclusively fixed on a polymer solid by coating a polyvinyl alcohol film and repeating freezing and thawing is brought in contact with the wastewater.

[Claim 4]

The method of removing phosphoric acid contained in wastewater according to claim 2 or 3, wherein the polymer solid is treated with coating by arginic acid.

[Claim 5]

A method of removing phosphoric acid contained in wastewater, wherein an inclusively fixed carrier in which calcium and magnetite are inclusively fixed on a polymer solid having an anionic group is brought in contact with wastewater, and calcium is diffused from the inclusively fixed carrier to prepare calcium apatite by reaction with the phosphoric acid in the wastewater.

[Claim 6]

The method of removing phosphoric acid contained in wastewater according to claim 5, wherein calcium or calcium hydroxide is kneaded with acetylated starch to be molded, and then the inclusively fixed carrier in which calcium is inclusively fixed on a polymer solid by coating a polyvinyl alcohol film containing magnetite is brought in contact with the wastewater.

[Claim 7]

The method of removing phosphoric acid contained in wastewater according to claim 6, wherein the inclusively fixed carrier in which

calcium is inclusively fixed on a polymer solid by coating a polyvinyl alcohol film and repeating freezing and thawing is brought in contact with the wastewater.

[Claim 8]

The method of removing phosphoric acid contained in wastewater according to claim 6 or 7, wherein the polymer solid is treated with coating by arginic acid.

[Claim 9]

The method according to any one of claims 1 to 4, further comprising mechanically shaking the polymer solid containing calcium to control the surface adhesion and diffusion of calcium.

[Claim 10]

The method according to any one of claims 5 to 8, further comprising mechanically or electromagnetically shaking the polymer solid containing calcium and magnetite to control the surface adhesion and diffusion of calcium.

[Claim 11]

The method according to any one of claims 1 to 8, further comprising recovering calcium apatite prepared in running water.

[Claim 12]

The method according to claim 9 or 10, further comprising recovering calcium apatite prepared.

[Claim 13]

An inclusively fixed carrier for removing phosphoric acid in wastewater, wherein calcium is supported on a polymer solid having an anionic group.

[Claim 14]

The carrier according to claim 13, wherein magnetite is contained in the polymer solid having an anionic group.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The invention of the present application relates to a method of removing phosphoric acid in domestic wastewater, industrial wastewater and the like. More specifically, the invention of the present application relates to removal of phosphoric acid from various wastewaters such as domestic wastewater, which are discharged from food industries, production fields in agriculture and the like.

[0002]

[Prior Art and Problems thereof]

The concentration of phosphoric acid in domestic wastewater is about 2 to 3 mg/L, but the removal of phosphoric acid in the domestic wastewater is an important subject for preventing eutrophication of rivers, lakes and marshes together with the necessity for removing phosphoric acid from the wastewaters of food industries, production fields in agriculture and the like.

[0003]

Studies for removing phosphoric acid have been promoted hitherto for such subjects. Then, there is proposed a method for reacting phosphoric acid in a solution, which contains calcium excessively to remove phosphoric acid. However, since the conventional method is a method of adding a calcium solution by a pump or the like to waste liquid

containing phosphoric acid, there has been a problem that calcium cannot be easily added in domestic drainage canals.

[0004]

[Means for Solving the Problems]

Then, the inventors of the present application has originated a process for gradually diffusing calcium by a carrier including calcium and adding it to wastewater in a drainage canal, in order to solve the problems of a prior art as describe above and to make it easy to add calcium in wastewater.

[0005]

Namely, the present invention provides a method of removing phosphoric acid contained in wastewater, wherein an inclusively fixed carrier in which calcium is inclusively fixed on a polymer solid having an anionic group is brought in contact with the wastewater, and calcium is diffused from the inclusively fixed carrier to prepare calcium apatite by reaction with the phosphoric acid in the wastewater.

[0006]

Further, the present invention provides a method of removing phosphoric acid contained in wastewater, wherein an inclusively fixed carrier in which calcium and magnetite are inclusively fixed on a polymer solid having an anionic group is brought in contact with wastewater, and calcium is diffused from the inclusively fixed carrier to prepare calcium apatite by reaction with the phosphoric acid in the wastewater.

[0007]

Furthermore, the present invention provides a method of

mechanically shaking a polymer solid containing calcium to control the surface adhesion and diffusion of calcium, and additionally, a method of mechanically or electromagnetically shaking a polymer solid containing calcium and magnetite to control the surface adhesion and diffusion of calcium, a method of recovering calcium apatite prepared in running water, and a method of recovering calcium apatite prepared.

[0008]

Moreover, the present invention provides seventh an inclusively fixed carrier for removing phosphoric acid in wastewater, wherein calcium is supported on a polymer solid, and provides eighth an inclusively fixed carrier, wherein magnetite is contained in a polymer solid.

[0009]

[Mode for Carrying Out the Invention]

The present invention has characteristics as described above, and embodiments of the invention will be illustrated below.

[0010]

The present invention has characteristics as described above, and embodiments of the invention will be described below. The invention employs an inclusively fixed carrier in which calcium is supported on a polymer solid, in order to remove phosphoric acid in wastewater. The polymer solid in this case can more preferably contain magnetite, and may be various solids so far as they are superior in the supportability of calcium. For example, there are used a polymer having anionic groups such as a hydroxyl group and a carboxyl group, and various other polymers. Suitable examples of the polymer solid

include polyvinyl alcohol (PVA), a partially esterified polymer thereof, poly(acrylic acid), a partially esterified polymer thereof, starch powder, a partially acetylated body thereof, and other polysaccharides.

[0011]

It is not always necessary that magnetite provides magnetism to the polymer, and magnetite is contained in the polymer so that the carrier can be moved or shaken by the magnetic field generated by magnetic field generating means (for example, an electro-magnet or permanent magnet) arranged at the outside of a wastewater treatment vessel or a wastewater treatment region. These magnetites may be powder of ultra paramagnets and the like which are not mutually adhered when the magnetic field does not exist. For example, they are powder of metal oxides of iron and the like.

[0012]

With respect to the method of the present invention and the fixed carrier therefor, it is indicated as one aspect that supported calcium is reacted with phosphoric acid in waste waster on the surface of the fixed carrier or in a state in which it is dispersed in a liquid to prepare calcium phosphate, namely calcium apatite, which is separated and recovered as crystals.

[0013]

Since there is a possibility that the diffusion of calcium is inhibited in a state in which calcium phosphate crystals are adhered on the surface of the carrier, the adhesion of the crystals on the surface of the carrier can be prevented, for example, by covering the fixed carrier (1) with a net (2) having a large hole diameter as shown

in FIG. 1 and mechanically shaking it in a treatment vessel (3). Further, the adhesion of the crystals on the surface of the carrier can be similarly prevented in such a manner that magnetite is contained in the carrier of the polymer solid and the magnetic field is varied by the surrounding electro-magnets (4) to be shaken as shown in FIG. 2.

[0014]

From the viewpoint of controlling the diffusion speed of calcium, the diffusion speed can be also controlled by shaking the carrier by these methods. The calcium apatite crystals obtained can be utilized as a fertilizer and the like, and therefore it is desirable to recover them by a simpler method so as not to discharge them from a drainage canal. Various procedures are considered for the means. For example, as shown in FIG. 3, the calcium apatite crystals (7) can be easily separated from wastewater to be recovered by providing a precipitation vessel (6) at the terminal end portion of the drainage canal (5) as FIG. 3 and periodically collecting them. The dispersion or diffusion of calcium from the fixed carrier can be controlled by the concentration of PVA as the polymer of the fixed carrier and the like, the concentration of calcium, the thickness of the fixed carrier, the shaking speed of the fixed carrier, etc. It is indispensable to prevent inhibition to calcium diffusion in case where the reaction on the surface of the carrier occurs. The recycle of calcium phosphate as a fertilizer by a periodical recovery operation is possible by diffusing calcium in the carrier by a forced shaking, accumulating calcium apatite, which is a reaction product, in the precipitation vessel, and

periodically collecting it. Hereat, the polymer carrier containing calcium shall be periodically exchanged.

[0015]

Further, in the example of FIG. 3, the calcium-containing polymer carrier (1) is charged in a cage (8) or the like which is easily shaken, and immersed in a place where the wastewater of the drainage canal (5) flows, the precipitation vessel is provided at its post-stage, and the cage (8) or the like is designed to be able to be mechanically or electrically shaken. However, the method is not limited to the example. The fixed carrier may be a fixed bed or a flowing bed together with the establishment of an appropriate processing condition.

[0016]

Then, examples are shown as follow to more specifically illustrate the present invention.

[0017]

[Examples]

(Example 1)

Method of preparing fixed carrier containing calcium

With respect to the carrier of calcium, one (weight ratio) of calcium hydroxide or caustic lime per one of acetylated starch is kneaded, the mixture is extruded by a molding machine to be spheres or pellets having a size of 5 to 10 mm to be prepared, and this is dropped in a 10 to 15% PVA solution to be covered with a thin film.

[0018]

It is appropriate that the average molecular weight of PVA is about 2000 and the degree of saponification is 95% or more. A 10 to

15% by weight of PVA solution is prepared to be used. Since the PVA molecule in an aqueous solution has a nature of discharging water molecule from the polymer structure and enforcing the structure when freezing and thawing are repeated, the nature is utilized. Specifically, the PVA solution is frozen at a low temperature of about -20℃ for 24 to 48 hours, the polymerization of PVA is promoted by repeating this operation 2 to 3 times, and the physical strength is enhanced. The acetylation substitution degree of the acetylated starch and the size of porous gels of the PVA polymer which are obtained by the operation control the discharge speed of calcium ion.

[0019]

Further, since arginic acid ion has a nature of forming a polymer by being bonded with calcium ion to be made insoluble, the nature can be used for covering the surface of the polymer solid. Specifically, the above-mentioned polymer solid is dropped in a 0.5 to 5% by weight of arginic acid solution, or the 0.5 to 5% by weight of arginic acid solution is sprayed on the surface of the polymer solid and this is dropped in a saturated solution of calcium chloride. The calcium arginate thus prepared is insoluble in water, a coating film is prepared on the arginate by the 10 to 15% PVA solution, and freezing is repeated 2 to 3 times at a low temperature of about -20℃ to prepare the fixed carrier containing calcium.

[0020]

When magnetite is used, it is desirable that 1.5 to 3.0 g of magnetite is preliminarily mixed in 50 to 100 mL of the PVA solution before polymerization by freezing or the like and the mixture is used.

(Example 2)

An inclusive fixed carrier was prepared by supporting calcium as in Example 1. A solution having an initial concentration of phosphoric acid of 3 mg/L was treated using the carrier.

[0021]

FIG. 4 shows the relation between the treatment time and the variation of the concentration of phosphoric acid in case of not adding calcium chloride as seed crystals, and FIG. 5 shows that in case of adding seed crystals. As a result, it was confirmed that the concentration of phosphoric acid can be set to about 0.1 to 1 mg/L. Thus, a removal rate of about 80% to 90% can be expected because the concentration of phosphoric acid is usually about several mg/L in a domestic drainage canal. Even if the concentration of phosphoric acid is higher than several mg/L, it is considered that the final concentration is about 0.5 mg/L.

[0022]

[Effect of the Invention]

According to the present invention, there are obtained superior effects that (1) the addition of calcium can be easily carried out by inclusively fixing calcium on a polymer, (2) the surface adhesion and diffusion of calcium can be controlled by electrically or mechanically shaking the polymer containing magnetite, and (3) the calcium apatite crystals can be separated and recovered from wastewater by periodically recovering them at a precipitation vessel provided at the terminal end portion of the drainage canal, and the reutilization of calcium phosphate as a fertilizer becomes easy, in the crystallization

operation of selectively removing phosphoric acid in wastewater in the drainage canal.

[Brief Description of Drawing]

[FIG. 1]

FIG. 1 is a sectional view exemplifying a system of mechanical shaking.

[FIG. 2]

FIG. 2 is a sectional view exemplifying a shaking system using an electro-magnet.

[FIG. 3]

FIG. 3 is a schematic view of the construction exemplifying a treatment system in which a precipitation vessel is provided.

[FIG. 4]

FIG. 4 is a view showing an example of a treatment result in case where no seed crystal exists.

[FIG. 5]

FIG. 5 is a view showing an example of a treatment result in case where seed crystals exist.

[Description of Codes]

1 Fixed carrier

2 Net

3 Treatment vessel

4 Magnet

5 Drainage canal

6 Precipitation vessel

7 Calcium apatite crystals

8 Cage

Fig.1

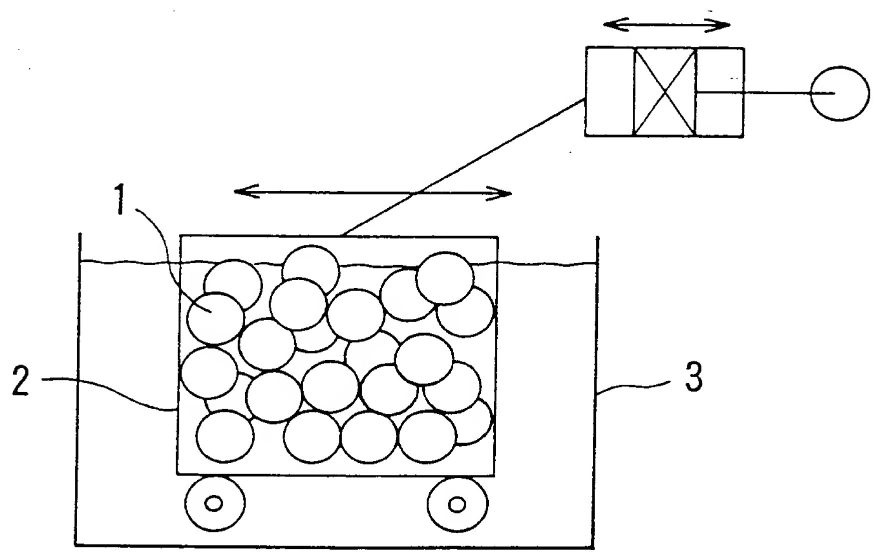


Fig.2

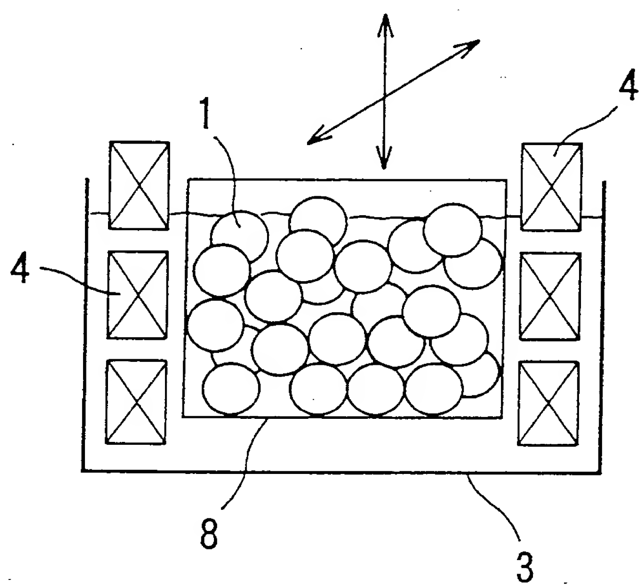


Fig.3

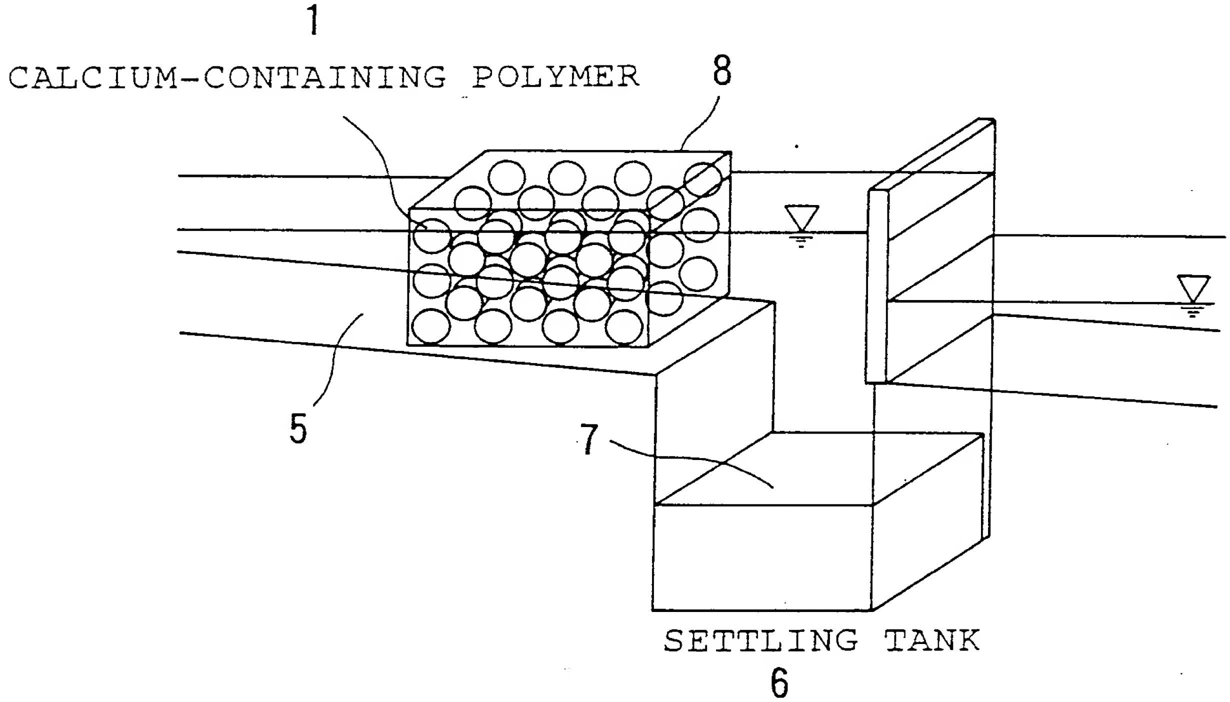


Fig.4

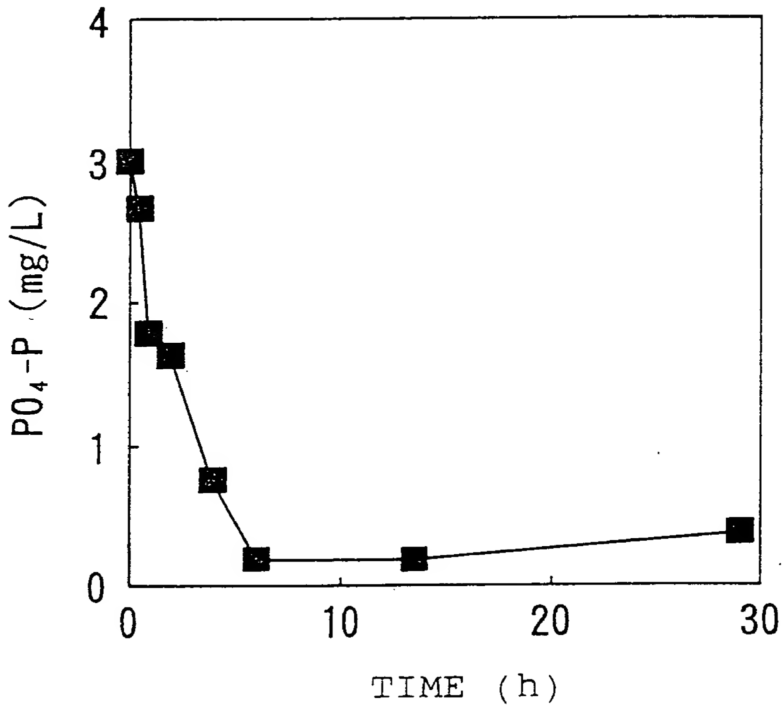
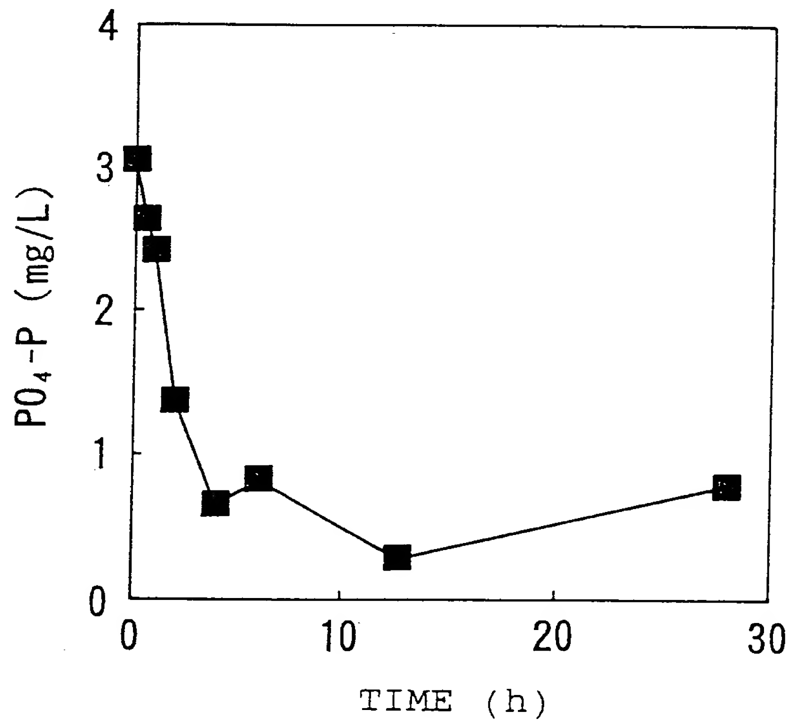


Fig.5



Encl. 2

JP-A-11-216479

[Title of the Invention]

Composition for collecting phosphoric acid ion

[Abstract]

[Object] An object of the present invention is to provide practical means for collecting and recovering phosphoric acid ions which are contained in water of drainage, rivers, lakes, marshes and the like and cause eutrophication, in a form capable of reutilization.

[Constitution] The practical means for collecting and recovering phosphoric acid ions contained in water, in a form capable of reutilization, which the present invention provides is means in which the powder of calcium carbonate and bentonite being a clay containing montmorillonite as a main clay mineral is reacted with water soluble polymer compounds such as polyvinyl alcohol to prepare a water-resistant particle composition, and the water-resistant particle composition is charged in a column or a bag of net and brought in contact with water containing phosphoric acid ions of drainage, rivers, lakes, marshes and the like, and thereby phosphoric acid ions in water are collected in a form of calcium phosphate which can be recycled.

Encl. 2

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特開平11－216479

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1/28		1/28	Ｐ

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(54)【発明の名称】　リン酸イオン捕集用組成物

(57)【要約】

【目的】本発明の目的は、排水、河川、湖沼等の水中に含まれ、富栄養化の原因になるリン酸イオンを再利用可能な形で捕集回収する実用手段を提供することである。

【構成】本発明が提供する水中のリン酸イオンを再利用可能な型で捕集回収する実用手段は、モンモリロナイトを主粘土鉱物とする粘土であるベントナトと炭酸カルシュウムの粉末をポリビニルアルコール等の水溶性高分子化合物と反応させて、耐水性の粒状組成物を作り、その耐水性粒状組成物をカラムまたは網の袋に入れて排水、河川、湖沼等のリン酸イオンを含む水と接触させることで、これら水中のリン酸イオンを再利用可能なリン酸カルシュウム塩という形で捕集するものである。

【特許請求の範囲】

【請求項１】モンモリロナイトを主粘土鉱物とする粘土であるベントナイトと粉末の炭酸カルシュウムの混合物に、水溶性高分子化合物の水溶液を加え、造粒しまたは造粒せずに乾燥し、耐水性にした後、砕きまたは砕かずに粒状にした、水中のリン酸イオン捕集用組成物。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、水中のリン酸イオンを再利用可能な形で回収する組成物に関するものであり、環境保護、農業の分野で利用されるものである。

【０００２】

【従来の技術】従来、鉄材を排水中に浸漬して、鉄表面から溶出する鉄イオンと排水中のリン酸イオンを結合させて難溶性のリン酸鉄塩として沈殿させる方法が提案されている。この方法では、貴重な資源としてのリン酸の回収・再利用は考えられていない。従来、排水中は勿論、河川、湖沼に存在し、富栄養価をもたらし、水質の悪化の主原因の一つになっているリン酸イオンを再利用可能な形で回収する実用的方法は存在しない。

【０００３】

【発明が解決しようとする課題】従来実用技術として存在しない、排水、河川、湖沼中のリン酸イオンを再利用可能な形で捕集、回収する方法を提供することを課題とした。

【０００４】

【課題を解決するための手段】前述の課題を解決するための手段について鋭意研究した結果、本発明者が到達した手段は、モンモリロナイトを主粘土鉱物とする粘土であるベントナイトと炭酸カルシュウム粉末の混合物と水溶性高分子化合物より成る、耐水性複合体の粒状組成物を用いて、水中のリン酸イオンを捕集する方法である。本発明について更に詳しく説明すると、ベントナイトと炭酸カルシュウム粉末の混合物に水溶性高分子化合物の水溶液を加えて混合した後、造粒して乾燥し耐水性の粒状組成物を得る方法を採っても良く、また、ベントナイトと炭酸カルシュウム粉末の混合物に水溶性高分子化合物の水溶液を加え混合した後、乾燥したものを砕いて、耐水性の粒状組成物を得る方法を採用しても良い。粒状組成物の粒径は１．０ｍｍから５．０ｍｍ位が扱い易いが、この範囲に限るものではない。また、予めベントナイトと炭酸カルシュウム粉末の水懸濁液を作っておいて、その中へ水溶性高分子化合物の水溶液を加える方法を採用して、反応物を造粒－乾燥、または、乾燥－粉砕工程をとおしても、目的とする耐水性の粒状組成物が得られる。乾燥の方法としては、通常の加熱乾燥、熱風乾燥の他、凍結乾燥を採用することが可能である。

【０００５】本発明による、水中のリン酸イオン捕集用の粒状組成物中に含まれるベントナイトの割合は９８．５から５５．０重量%で、残りの部分が炭酸カルシュウム粉末と水溶性高分子化合物である。使用するベントナイトの置換性カチオンはＮａイオンでもＣａイオンでも良い。ただ、ベントナイトの陽イオン交換能は、５０ｍｇ当量／１００ｇ・粘土以上であることが望ましい。炭酸カルシュウム粉末の量は、１．０から５４．０重量%の範囲で粒状組成物に含まれるが、特に、１．０から２５．０重量%含まれたものが取り扱い上良い。また、炭酸カルシュウム粉末の粒径は、１００メッシュのフルイをとおしたものが望ましいが、その範囲に限らない。バインダーとしての水溶性高分子化合物としては、ポリビニルアルコールとそのシラノール変性物が、粒状組成物に耐水性を付与するのに優れているものである。水溶性高分子化合物が粒状組成物の中に含まれる割合は、０．５から５．０重量%が良い。バインダーの含量は、粒状組成物の膨潤度に関わる。バインダーとしての水溶性高分子化合物としては、上述のポリビニルアルコール系以外に、ポリアクリル酸ソーダ、アルギン酸ソーダ等のポリアニオン系水溶性化合物をポリビニルアルコール系化合物に混合して用いても良い。

【０００６】

【作用】次に、本発明の作用について説明する。１９４０年代のわが国の環境保護政策により、排水中のＢＯＤ、ＣＯＤ値が規制され、河川、湖沼、港湾水域での水質の汚染度は大きく進まなくなっている。しかし、河川、湖沼に関するかぎり、窒素化合物やリン化合物による富栄養価は進んでいるといえる。それをリン酸イオンに関していうと、有効に水中から除去する実用的な方法が無いのが現状である。また、リン酸イオンは植物に必須のものであるが、資源としては限られており貴重なものである。また、リン酸イオンが自然条件下で植物に利用されるのは、１価か２価のカチオンとの化合物であり、鉄やアルミニウムとの化合物は植物には利用され難いのである。それ故、水中のリン酸イオンを回収する際、それが再利用を目的とするならば、１価か２価のカチオンとの化合物と言う形をとる事が望ましい。幸い、リン酸イオンはカルシュウムイオンと反応して容易に、リン酸カルシュウム塩を作り、このものはアルカリ性下では、水に難溶性である。本発明者が発明したリン酸イオン捕集用の粒状組成物は、その中にリン酸イオンをカルシュウム塩の形で捕集する。そして、この粒状組成物の中では、ｐＨが常にアルカリ側に保たれているので、捕集されたリン酸カルシュウム塩は水に溶けずに回収されるのである。回収されたリン酸カルシュウム塩を含む粒状組成物は、リン酸肥料として、また、土壌改良材として有効利用できるのである。

【０００７】

【実施例】１．陽イオン交換能が６６ｍｇ当量／１００ｇのＣａ－ベントナイトの２０％水懸濁液を５００ｍｌ作成し、それに１００メッシュのフルイをとおした炭酸カルシュウム粉末２ｇを入れ良く混合した後、重合度１

７００、鹸化度９８ｍｏｌ％のポリビニルアルコールの１０％水溶液を３０ｍｌ加え混合、反応させて後、反応物をプラスチックのバットに、厚さ１ｃｍになるように流し込み、６０℃の熱風乾燥機で乾燥した。この乾燥物を砕き、フルイにかけて粒径２．０ｍｍから５．０ｍｍの耐水性粒状組成物を約７０ｇ得た。これを組成物１とした。

２．陽イオン交換能が６６ｍｇ当量／１００ｇのＣａ－ベントナイトの２０％水懸濁液を５００ｍｌ作成し、それに１００メッシュのふるいをとおした炭酸カルシュウム粉末２０ｇを入れ良く混合した後、実施例１で使用したポリビニルアルコールの１０％水溶液を５０ｍｌ加え混合、反応させた。後は、実施例１と同じ工程を採って、耐水性粒状組成物約６５ｇを得た。これを組成物２とした。

３．実施例１で使用したのと同じＣａ－ベントナイト１００ｇと矢張り実施例１で使用したのと同じ炭酸カルシュウム粉末８ｇを１０００ｍｌのビーカーに入れ粉末同意で混合し、それに実施例１で使用したものと同じポリビニルアルコールの２％水溶液を１５０ｍｌ加えて良く混合し反応させた後、凍結乾燥をした。この凍結乾燥物を砕き、フルイにかけて粒径２．０ｍｍから５．０ｍｍの耐水性粒状組成物を約７５ｇ得た。これを組成物３とした。

４．実施例２と同じ手順でサンプルを調製する際に、炭酸カルシュウム粉末を加えずに耐水性粒状組成物を作＊り、それを組成物４とした。

５．実施例１と同じ手順でサンプルを調製する際に、バインダーとしてのポリビニルアルコール水溶液を加えず粒状組成物を作り、それを組成物５とした。

６．実施例１、２、３、４、５で作成した組成物１、２、３、４、５を１ｍｍの目のナイロン製の網をコックの上に敷いた５０ｍｌ容ビュレットに２５ｇずつ入れ、その上にもナイロン製の網を入れて組成物の表面を覆った。各ビュレットにｐＨ７．０の脱塩水を３０ｍｌずつ注ぎ込み、室温で２４時間置いた後、コックを開いて水を流し出した。この際、組成物５は、粒状状態を消失してしまい、その後のリン酸イオンの捕集実験には適さなくなったので実験系から除外した。次に、水を抜いた各ビュレットにリン酸イオン濃度が６．０ｐｐｍになるように調製したリン酸第一カリ水溶液を３０ｍｌずつ注ぎ込み５分間静置した後、コックを調節して、５から６分かけて、リン酸塩水溶液を滴下させて回収し、そのリン酸イオン濃度を比色法（Ｄｅｎｉｇｅｓ法）で測定した。繰り返し実験では、注ぎ込んだリン酸塩水溶液をビュレットから滴下し回収が終わると、直ぐに新しいリン酸第一カリの水溶液３０ｍｌをビュレットに注ぎ込み、５分間静置した後５から６分かけて耐水性粒状組成物層を通過した液を回収し、そのリン酸イオン濃度の測定に供した。リン酸イオンの繰り返し捕集実験は３回行ったが、その結果を表１に示した。

表　１

耐水性粒状組成物のリン酸イオンの繰り返し捕集能

－流出液のリン酸イオン濃度－（ｐｐｍ）

組成物	繰り返し回数（回目）		
	１	２	３
１	０．１	２．０	４．３
２	０．１	１．５	２．１
３	０．１	０．６	１．２
４	０．１	５．４	５．７

表１の結果から明らかなように本発明による、水中のリン酸イオン捕集用粒状組成物は水中のリン酸イオンを効率良く捕集回収出来ることが分かった。

７．各粒状組成物２５ｇをそれぞれ２００ｍｌ容ビーカーに入れ、実施例５で用いたリン酸第一カリの水溶液を９０ｍｌ加え、スターラーで１時間かき混ぜたのち、各区ビーカーの上澄液を採取してそのリン酸イオン濃度を測定した結果、組成物１、２、３、４すべての試験区で、リン酸イオン濃度は０．１ｐｐｍであった。

【０００８】

【発明の効果】実施例で示したように、本発明は水中のリン酸イオンを再利用可能な、リン酸カルシュウム塩という形で捕集する耐水性粒状組成物を提供することが出来た。この耐水性粒状組成物を充填したカラムに、リン酸イオンを含む排水を流すことで、排水中のリン酸イオンを捕集することができる。また、この耐水性粒状組成物を網の袋に入れて河川に設置することで、河川に含まれるリン酸イオンが捕集出来る。また、網の袋を船の後ろに吊るして、湖沼を巡ることにより、湖沼の水に含まれるリン酸イオンが捕集回収可能なことが実施例の結果から分かった。